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PATENTKANTOOR  
REPUBLIC OF SOUTH AFRICA

DEPARTEMENT VAN HANDEL  
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**Certificate**

PATENT OFFICE  
REPUBLIEK VAN SUID-AFRIKA

DEPARTMENT OF TRADE AND  
INDUSTRY

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This is to certify that

REC'D 12 DEC 2003

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the documents annexed hereto are true copies of:

Application forms P.1 and P.3, provisional specification and  
drawings of South African Patent Application No. **2003/1355**  
as originally filed in the Republic of South Africa on **18 February**  
**2003** in the name of **SOUTH AFRICAN NUCLEAR ENERGY**  
**CORPORATION LIMITED** for an invention entitled: "**OXYFLUO-**  
**RINATION**".

**PRIORITY DOCUMENT**  
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RULE 17.1(a) OR (b)

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PRETORIA

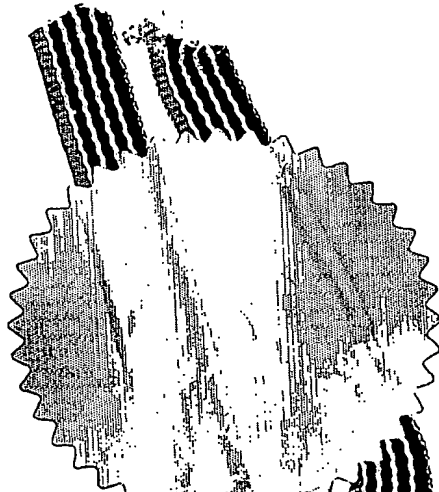
in die Republiek van Suid-Afrika, hierdie  
in the Republic of South Africa, this

13th

dag van  
day of

November 2003

Registrateur van Patente



REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
APPLICATION FOR A PATENT AND  
ACKNOWLEDGEMENT OF RECEIPT  
(Section 30(1) Regulation 22)

FORM P.1  
(to be lodged in duplicate)

REPUBLIC OF SOUTH AFRICA

REVENUE

18 2 03

R 000.00

THE GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT  
ON THE BASIS OF THE PRESENT APPLICATION FILED IN DUPLICATE

21 01 PATENT APPLICATION NO 2003/1355

REPUBLIC OF SOUTH AFRICA  
A&A-RECEIVED 5607 AS/dec

71 FULL NAME(S) OF APPLICANT(S)

SOUTH AFRICAN NUCLEAR ENERGY CORPORATION LIMITED

ADDRESS(ES) OF APPLICANT(S)

Pelindaba, District Brits,  
Gauteng Province, Republic of South Africa

54 TITLE OF INVENTION

"OXYFLUORINATION"

Only the items marked with an "X" in the blocks below are applicable.

☐ THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. The earliest priority claimed is

Country:

No:

Date:

☐ THE APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO 21 01

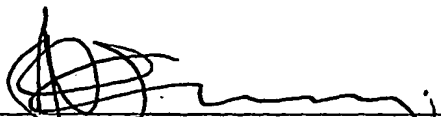
☐ THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON  
APPLICATION NO 21 01

THIS APPLICATION IS ACCOMPANIED BY:

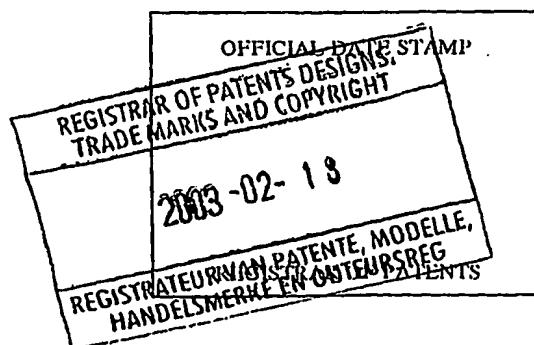
- ☒ Two copies of a provisional specification of 46 pages
- ☒ Drawings of 2 sheets
- ☐ Publication particulars and abstract (Form P.8 in duplicate) (for complete only)
- ☐ A copy of Figure of the drawings (if any) for the abstract (for complete only)
- ☒ An assignment of invention
- ☐ Certified priority document(s). (State quantity)
- ☐ Translation of the priority document(s)
- ☐ An assignment of priority rights
- ☐ A copy of Form P.2 and the specification of RSA Patent Application No 21 01
- ☒ Form P.2 in duplicate
- ☒ A declaration and power of attorney on Form P.3
- ☐ Request for ante-dating on Form P.4
- ☐ Request for classification on Form P.9
- ☐ Request for delay of acceptance on Form P.4
- ☐ Extra copy of informal drawings (for complete only)

74 ADDRESS FOR SERVICE: Adams & Adams, Pretoria

Dated this 18th day of February 2003

  
AV VR SCHWEIZER  
ADAMS & ADAMS  
APPLICANT'S PATENT ATTORNEYS

The duplicate will be returned to the applicant's address for service as  
proof of lodging but is not valid unless endorsed with official stamp



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REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
DECLARATION AND POWER OF ATTORNEY  
(Section 30 - Regulation 8, 22(i)(c) and 33)

FORM P.3

PATENT APPLICATION NO		A&A Ref: V15607 AS/dcd	LODGING DATE	
21	01	2003 / 1355	22	18 February 2003

FULL NAME(S) OF APPLICANT(S)	
71	SOUTH AFRICAN NUCLEAR ENERGY CORPORATION LIMITED

FULL NAME(S) OF INVENTOR(S)	
72	1) CARSTENS, Pieter Andries Blatt 2) LOUW, Izak de Villiers

EARLIEST PRIORITY CLAIMED	COUNTRY	NUMBER	DATE			
	33	NIL	31	NIL	32	NIL

NOTE: The country must be indicated by its International Abbreviation - see schedule 4 of the Regulations

TITLE OF INVENTION	
54	"OXYFLUORINATION"

I/we, Nicholas Lazarus Mxolisi NGWENYA

hereby declare that :-

1. ~~I/we am/are the applicant(s) mentioned above;~~

\*\* 2. I/we have been authorized by the applicant(s) to make this declaration and have knowledge of the facts herein stated in the capacity of Chief Legal Adviser - Legal Services of the applicant(s);

\*\*\* 3. the inventor(s) of the abovementioned invention is/are the person(s) named above and the applicant(s) has/have acquired the right to apply from the inventor Carstens in terms of Section 28 of Act 46 of 1999 and by virtue of an assignment from the inventor Louw;

4. to the best of my/our knowledge and belief, if a patent is granted on the application, there will be no lawful ground for the revocation of the patent;

\*\*\*\* 5. ~~this is a convention application and the earliest application from which priority is claimed as set out above is the first application in a convention country in respect of the invention claimed in any of the claims; and~~

6. the partners and qualified staff of the firm of ADAMS & ADAMS, patent attorneys, are authorised, jointly and severally, with powers of substitution and revocation, to represent the applicant(s) in this application and to be the address for service of the applicant(s) while the application is pending and after a patent has been granted on the application.

SIGNED THIS 11<sup>th</sup> DAY OF FEBRUARY 2003

  
For and on behalf of: SOUTH AFRICAN NUCLEAR ENERGY CORPORATION LIMITED

Full Names: Nicholas Lazarus Mxolisi NGWENYA

Capacity: Chief Legal Adviser - Legal Services

(no legalization necessary)

\* In the case of application in the name of a company, partnership or firm, give full names of signatory/signatories, delete paragraph 1, and enter capacity of each signatory in paragraph 2.

\*\* If the applicant is a natural person, delete paragraph 2.

\*\*\* If the right to apply is not by virtue of an assignment from the inventor(s), delete "an assignment from the inventor(s)" and give details of acquisition of right.

\*\*\*\* For non-convention applications, delete paragraph 5.

REPUBLIC OF SOUTH AFRICA

## REGISTER OF PATENTS

PATENTS ACT, 1978

OFFICIAL APPLICATION NO.		LODGING DATE: PROVISIONAL		ACCEPTANCE DATE	
22	01/2003/1355	22	18 FEBRUARY 2003	47	
INTERNATIONAL CLASSIFICATION		LODGING DATE: COMPLETE		GRANTED DATE	
FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)					
71	SOUTH AFRICAN NUCLEAR ENERGY CORPORATION LIMITED				
APPLICANTS SUBSTITUTED:				DATE REGISTERED	
71					
ASSIGNEE(S)				DATE REGISTERED	
71					
FULL NAME(S) OF INVENTOR(S)					
72	CARSTENS; Pieter Andries Blatt LOUW, Izak de Villiers				
PRIORITY CLAIMED		COUNTRY		NUMBER	
N.B. Use International Abbreviation for country (See Schedule 4)		33	NIL	31	NIL
TITLE OF INVENTION					
54	"OXYFLUORINATION"				
ADDRESS OF APPLICANT(S)/PATENTEE(S)					
Pelindaba, District Brits, Gauteng Province, Republic of South Africa					
ADDRESS FOR SERVICE				A & A REF:	
74	ADAMS & ADAMS, Pretoria			V15607 AS/dcd	
PATENT OF ADDITION TO NO.		DATE OF ANY CHANGE			
61					
FRESH APPLICATION BASED ON		DATE OF ANY CHANGE			

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PRETORIA

REPUBLIC OF SOUTH AFRICA  
Patents Act, 1978

## PROVISIONAL SPECIFICATION

(Section 30 (1) - Regulation 27)

21	01	OFFICIAL APPLICATION NO
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22	LODGING DATE
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**2003 / 1355**

18 February 2003

71	FULL NAME(S) OF APPLICANT(S)
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SOUTH AFRICAN NUCLEAR ENERGY CORPORATION LIMITED

72	FULL NAME(S) OF INVENTOR(S)
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CARSTENS, Pieter Andries Blatt  
LOUW, Izak de Villiers

54	TITLE OF INVENTION
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"OXYFLUORINATION"

**THIS INVENTION** relates, broadly, to oxyfluorination. More particularly the invention relates to a process for the oxyfluorination of a solid.

According to the invention, in the oxyfluorination of at least part of the surface of a solid, there is provided a process whereby the oxyfluorination is effected by exposing the surface of the solid at least in part to an oxyfluorinating atmosphere which is a gas/vapour mixture which comprises:

- at least one fluorine-containing gas which reacts with the exposed surface;
- at least one oxygen-containing gas which reacts with the exposed surface;
- and
- water vapour,

the oxyfluorinating atmosphere acting to oxyfluorinate the exposed surface to provide it with a beneficial property and the water vapour acting to enhance the beneficial property when compared with the action of an oxyfluorinating atmosphere comprising the same fluorine-containing gas, the same oxygen-

containing gas and any other constituents in the same proportions, but omitting the water vapour.

The beneficial property with which the exposed surface is provided by the oxyfluorination is the activation of the surface to render it more amenable to adhesive bonding to materials such as inks or printed pigments printed thereon, coating materials deposited thereon by metallization such as vapour phase metallization, and in particular glues and adhesives, ceramics and paints, and to render it more amenable to adhesive bonding to cementitious materials or the like, in the reinforcement of such materials by oxyfluorinated reinforcing materials, for example in the production of composite products.

Thus, more particularly, in the formation of an adhesive bond between two components, by bringing the components into contact with each other with one of the components in a flowable or mouldable state and the other of the components in solid form, and causing or allowing the flowable or mouldable component to set or cure in contact with the solid component, thereby to bond adhesively to the solid component to form an adhesive bond therebetween so that the solid component reinforces and strengthens the set component, the process of the present invention may act to enhance adhesion of the set component to the solid component, the process comprising the step, prior to bringing the components into contact with each other, of subjecting the solid component to surface activation thereof, the surface activation being effected by said exposing at least that part of the surface of the solid component which is to be bonded to

the flowable or mouldable component by the setting or curing thereof, to said atmosphere which acts as an activating atmosphere which activates the exposed surface part by oxyfluorination in the presence of the water vapour which acts to promote the beneficial property of a high bond strength between the components.

It is expected that the coating aspect of the enhanced bonding of the present invention will have substantial utility in the coating of polymeric substrates, particularly those which are refractory or resistant to coating. Examples of such polymers are hydrocarbon polymers which contain only carbon and hydrogen as constituents, polymers which contain, in addition to carbon and hydrogen as constituents, constituents other than carbon and hydrogen and which polymers comprise hydrogen atoms which can be replaced by fluorine atoms, and mixtures or blends of such polymers. Such polymers can be used for the mass production of motor-vehicle parts, such as bumpers or buffers, in which case it is important and desirable to be able to coat them with durable paint coatings, which adhere strongly thereto. However, the coating aspect may involve coating solid substrates which are not of polymeric materials, but which have surfaces which can be activated by the activating atmosphere to receive coatings, with desirable adhesion thereto.

For the purpose of this specification, it should be noted that the term "polymers" includes elastomers, and the term "polymeric" accordingly includes "elastomeric".



It is in turn expected that the reinforcing aspect of the enhanced bonding of the present invention will have substantial utility in the production of composite materials, structures and/or artifacts wherein a cementitious matrix is strengthened or reinforced by reinforcing material. In these cases the component in the flowable mouldable state is a typically cementitious slurry which is caused or allowed to set and/or cure in contact with the solid component which acts as a reinforcing component, to form a set cementitious matrix which adhesively adheres by means of a cementitious bond to the reinforcing component so that the matrix is strengthened and reinforced thereby. Such cementitious matrices have, typically, a relatively low tensile strength and/or a relatively low fracture toughness; whereas the reinforcing materials, typically, have a relatively high tensile strength and/or fracture toughness. The reinforcing material will thus be solid at ambient temperatures and may comprise particles such as granules, or, in particular, fibres, and may be in the form a polymeric material which is activated by the oxyfluorination.

As indicated above, examples of polymeric substrate materials include polymers which are polyhydrocarbons such as polypropylene, polyethylene, polystyrene, polypentene, polybutadiene, or the like, consisting only of carbon and hydrogen; and mixtures or blends of two or more such polymers, which may be selected from hydrocarbon homopolymers and copolymers such as block copolymers, random- or statistical copolymers and graft copolymers, and from higher polymers such as terpolymers, containing only carbon and hydrogen. Instead, the polymeric substrate material may comprise polymers of olefins which

do not only contain carbon and hydrogen. Furthermore, depending on their end use, said hydrocarbon polymers may be blended or mixed with application-specific additives which do not contain only carbon and hydrogen, and/or the hydrocarbon polymers may be blended or mixed with polymers of olefins which do not contain only carbon and hydrogen, but which contain other constituents, each of which polymer groups again being homopolymers or copolymers such as block copolymers, random- or statistical copolymers, graft copolymers, or higher polymers such as terpolymers, for example polyamides (nylons), aramids (kevlar) or acrylonitrile butadiene styrenes (ABS polymers), one or more of which olefins is a polymer having a constituent other than carbon or hydrogen, provided that the polymer containing the application-specific additive or having a constituent other than carbon or hydrogen comprise hydrogen atoms which are replaceable by fluorine atoms, before activation thereof in accordance with the process of the present invention. Blends which are employed as substrates may be formed by physically blending their constituents or by polymerizing their constituents together in a reactor. Whatever the nature of the substrate, it should, however, contain hydrogen surface atoms which are replaceable by fluorine atoms and preferably also by oxygen atoms during oxyfluorination of its surface.

When the enhanced bonding of the present invention is utilized for the strengthening and reinforcement of a cementitious matrix, the reinforcing component material is conveniently a polypropylene or a polyethylene, such as an ultra-high mass polyethylene (UHMPE), or higher polymers such as nylons, kevlar or ABS polymers, or even materials other than polymers, but which have surfaces

which can be activated by the activating atmosphere of the present process, an example being carbon. When the enhanced bonding of the present invention is utilized for the coating of solid components in the form of polymeric substrates, the substrate material is conveniently an olefinic polymer such as a polypropylene homopolymer, a high-density polyethylene (HDPE) or a reactor-grade thermoplastic olefin (RTPO).

Exposing the surface of the solid to the atmosphere comprising the gas/vapour mixture of the present invention will be under conditions of temperature and pressure, and for a reaction time, selected to provide the exposed surface with desired properties. The fluorine-containing gas may be fluorine ( $F_2$ ) itself, or it may be made up of one or more other suitable fluorine-gaseous compounds, examples of which are fluorinated noble gases such as  $XeF_2$ , or fluorohalogens such as  $ClF$ ,  $ClF_3$ ,  $BrF$ ,  $BrF_3$ ,  $BrF_5$ , and  $IF_7$ , or oxides of fluorine such as  $OF_2$  or  $O_2F_2$  so that, in other words, the activating atmosphere may include a fluorine-containing gaseous compound selected from the group consisting of  $F_2$ ,  $XeF_2$ ,  $ClF$ ,  $ClF_3$ ,  $BrF$ ,  $BrF_3$ ,  $BrF_5$ ,  $IF_7$ ,  $OF_2$  or  $O_2F_2$  and mixtures of at least two such gases. The oxygen-containing gas may be selected from the group of oxygen-containing gaseous compounds consisting of  $O_2$ ,  $O_3$  and mixtures thereof. Optionally, the activating atmosphere may include, in addition to any fluorine-containing gaseous compound, any oxygen-containing gaseous compound and any further reactive gas, also at least one inert - or diluent gas which is inert to, and does not react with, the reinforcing component surface, such as helium, argon or, in particular, nitrogen ( $N_2$ ). Thus, in particular, the activating atmosphere may be a mixture of

fluorine gas and wet or moist air containing water vapour, which can more correctly be regarded as humid air, the atmosphere having, as constituents,  $F_2$ ,  $O_2$ ,  $N_2$ , and water vapour. If desired, the gas/vapour mixture may have its activity enhanced by subjecting it before and/or during the exposure of the solid surface thereto, to ultra-violet (UV) radiation.

The reaction conditions may vary between relatively broad limits. Thus, exposing the solid surface to the activating atmosphere may be for a period of 0.10 seconds - 10 hours, e.g. 1 second - 1 hour, at a total pressure of the activating atmosphere of 0.1 kPa - 500 Kpa, e.g. 1 kPa - 200 kPa, and at a temperature of the surface of the solid and of the gas/vapour mixture of above  $0^\circ C$  at which the reinforcing component is solid, e.g.  $0^\circ C$  up to the melting point of the solid, if it melts rather than charring or decomposing. Furthermore, in the gas/vapour mixture, the fluorine-containing gas may have a partial pressure from as low as 0.01 kPa up to as high as 200 kPa, when the fluorine-containing gas is  $F_2$ . Preferably, thus, the activation is effected by exposing the solid surface to the activating gas/vapour mixture at a pressure of 1 - 200 kPa, more preferably 5 - 150 kPa, and at a temperature above  $0^\circ C$  and below the melting or charring/-decomposition temperature of the material of the solid, i.e. typically  $20-100^\circ C$ . Reaction times which are short have been found to be feasible, for example 0.1-60 seconds, typically 1 - 10 seconds or even 1 - 5 seconds.

The gas/vapour mixture may, in addition to its comprising a fluorine-containing gas, an oxygen-containing gas, water vapour and any inert or diluent

gas used, contain also at least one further reactive gas selected from halogens other than fluorine, such as chlorine ( $\text{Cl}_2$ ), bromine ( $\text{Br}_2$ ) or indeed iodine ( $\text{I}_2$ ) vapour, or selected from oxides of sulphur, oxides of nitrogen and oxides of carbon, interhalogen compounds or mixtures thereof. The proportion of the fluorine-containing gas in the gas/vapour mixture can vary within wide limits. Thus, the fluorine-containing gas may form 0.1 - 99.0% by volume of said mixture, typically 1 - 30% by volume thereof. Particularly preferred gas/vapour mixtures include those comprising 5 - 20% by volume of fluorinating gas such as  $\text{F}_2$  and 5 - 95% by volume oxygen ( $\text{O}_2$ ). The water vapour content of the gas/vapour mixture may be such that it has a relative humidity of 0.1 - 99%, preferably 30 - 90%, e.g. 50 - 80%.

In particular, the reaction may be such as to provide the exposed solid with a surface tension at 20°C of at least 40 mN/m. While the reaction may be such as to provide the exposed solid surface with a relatively low surface fluorine concentration, e.g. in the range of  $0.01 \mu\text{gF}/\text{cm}^2$  -  $50 \mu\text{gF}/\text{cm}^2$ , higher surface fluorine concentrations of above  $50 \mu\text{gF}/\text{cm}^2$  are obtainable, if desired. In a particular embodiment, the fluorine-containing gas may be  $\text{F}_2$ , being present in the gas/vapour mixture at a partial pressure of 0.01 kPa - 200 kPa, the exposing of the surface of the solid to the gas/vapour mixture being such as to provide the surface with a surface fluorine concentration of  $0.01 - 50 \mu\text{gF}/\text{cm}^2$ .

The process may include, prior to the activation step, the step of degreasing the solid to be oxyfluorinated, for example by washing the solid with

water and a detergent followed by rinsing it with water and then treating it with isopropanol or another suitable organic solvent such as those used in the motor trade for dislodging grease or oil. In a particular embodiment the method may include, prior to exposing of the surface, the step of degreasing the exposed surface.

Exposing the solid surface to the gas/vapour atmosphere may be in a reaction chamber or a reaction vessel, which has been flushed by means of such gas/vapour atmosphere, and may be carried out on a continuous basis or on a batchwise basis. If carried out on a continuous basis, exposing the solid surface to the atmosphere may be effected in in-line fashion by continuously transporting the solid through a reaction chamber, which may be open-ended, containing the atmosphere. The gas/vapour atmosphere may, as indicated above and if desired, be subjected to UV radiation, during the exposure of the solid thereto.

Naturally, routine experimentation will be carried out with regard to the various parameters such as gas/vapour atmosphere compositions and pressures, reaction times, temperatures, substrates or solids whose surfaces are activated, and the fluorine- and oxygen surface concentrations and surface tensions achieved thereon, to achieve optimum, or at least acceptable, results, bearing practical and economic considerations in mind.

With regard to the coating aspect of the present invention, applying the coating to the oxyfluorinated surface may be by painting e.g. spray-painting,

the oxyfluorinated surface with one of the following paints:-

a single-component base coat in an organic solvent; followed by

a clear two-component (top) coat in an organic solvent; or

a two-component pigmented top coat in an organic solvent or diluent.

A resin- and a hardener- (or catalyst) component of a two-component polyurethane or epoxy paint are typically contained in two separate tins. When the paint is required for spray painting the resin and the hardener are mixed in a specified ratio and then thinned to a spraying viscosity. This paint mixture has a limited life-time, usually a few hours. Single-component paints do not require or employ a hardener, and only need to be thinned to spraying viscosity.

The invention also extends to the products of the processes described herein. Thus, with regard to coating, the invention extends to a substrate such as polymeric substrate, whenever coated in accordance with the process of the present invention; and in accordance with the reinforcing of components, the invention extends to a composite material, structure and/or artifact which comprises a set cementitious matrix strengthened or reinforced by reinforcing material to which the cementitious matrix adheres, the matrix comprising a settable cementitious component which has set in contact with a reinforcing component to form a cementitious matrix in contact with a reinforcing material comprising said reinforcing component and which adheres thereto, by means of an adhesive bond, the reinforcing component having an oxyfluorinated surface to which the cementitious matrix adheres, the composite material, structure and/or artifact having been produced in accordance with the process of the present invention.

The invention will now be described, by way of illustrative example, with reference to the following Examples and with reference to the accompanying diagrammatic drawings, in which:

Figure 1 shows a three-dimensional view of a test sample used for the fibre pull-out tests described hereunder with reference to Examples 1 and 2 dealing with the reinforcing aspect of the present invention; and

Figure 2 shows a diagrammatic flow/block diagram illustrating details of the reactor employed for the coating aspect of the present invention.

## **REINFORCING OF COMPOSITES**

### **EXAMPLE 1 - INVENTION**

Monofilament polypropylene fibres were produced by direct extrusion to have a rectangular cross-section nominally of 0.5mm x 1.3mm, the fibres having a length of 40mm, a specific gravity of 0.91, a tensile strength of 120MPa and an elongation at break of 14%. The fibres were loaded under a humid ambient air atmosphere into a vacuum reaction vessel and the vessel was evacuated down to an absolute pressure of 15 kPa. The vessel was then loaded with a dry 20% F<sub>2</sub>/80%N<sub>2</sub> (by volume) gas mixture up to a pressure of 45 kPa at a temperature of 38°C, to form an oxyfluorinating atmosphere in accordance with the present invention. The fibres had their surfaces activated by oxyfluorination by allowing them to remain in contact with the activating atmosphere in the vessel for 2.5 hours at 38°C, after which the vessel was flushed with ambient air. During this contact the



surfaces of the polypropylene fibres were activated by oxyfluorination, in the presence of water vapour, by oxygen from the air at 15 kPa present in the vessel after evacuation, and by fluorine from the  $F_2/N_2$  gas mixture added, the water vapour also being derived from the air at 15 kPa remaining in the vessel after the evacuation and providing the activating gas at 45 kPa with a relative humidity of approximately 18%.

### EXAMPLE 2 - CONTROL

Example 1 was repeated except that the air at 15 kPa present in the vessel before loading of the  $F_2/N_2$  gas mixture was replaced by a dry mixture of 21%  $O_2/79\%N_2$  (by volume). This was effected by evacuation of the vessel down to a hard vacuum at effectively zero pressure for purposes of practical utility, followed in turn by loading of the  $O_2/N_2$  mixture into the vessel and loading of the  $F_2/N_2$  mixture into the vessel.

A highly flowable and readily castable and smoothable mortar slurry mix was prepared by mixing together ordinary Portland cement with dried natural river sand and water in a cement:water:sand mass ratio of 1:0.52:2. The river sand had a maximum particle size in the range of about 2-4.7mm and an average particle size in the range of about 0.6-1.5mm. Mixing was effected manually until the mixture was homogeneous. Fibre pull-out tests were then conducted on dumb-bell-shaped specimens, one of which is indicated by reference numeral 10 in Figure 1, prepared by casting fresh mortar mix into dumb-bell-shaped polymethylmethacrylate moulds. Each specimen had a thickness  $T$  of 20mm and a maximum

width W of 51mm, and had a waist 12 which divided it into two lobed parts 14. A plastics sheet 16 at the waist 12 separated the parts 14 from each other to prevent bonding therebetween. One of the monofilament fibres, after surface activation, was embedded at 20 in the specimen 12 to extend along its polar axis 18, with half (20mm) of its length embedded in each lobed part 14. The specimen was then allowed to set to form a set cementitious matrix in which the reinforcing component formed by the fibre 20 was embedded, adhesive cementitious bonding taking place between the fibre 20 and the matrix. The cast specimens were cured respectively for 7 and 28 days in water at a temperature of 21-25°C. The strength of the adhesive interfacial shear bond between the fibre 20 and the cementitious matrix was measured using a tensile testing machine equipped with a 500N transducer and a data-logging system, operating at a pull-out rate of 2mm/minute. The interfacial shear bond strength was calculated by dividing the maximum shear bond force attained by the bonding area of the fibre, i.e:

$$\text{Interfacial shear} = \frac{\text{maximum shear bond force}}{\text{length of fibre} \times (\text{width} + \text{thickness of fibre}) \times 2}$$

The units of the shear bond force and length are selected so that the interfacial shear bond strength is obtained in MPa. The fibre pull-out test results are presented in the following table, Table 1, for fibres produced by both Example 1 and Example 2, and in each case after 7 and 28 days' curing time respectively, five specimens being tested in each case.

**TABLE 1**

	<u>Shear bond strength (MPa)</u> <u>(7 days' curing )</u>		<u>Shear bond strength (MPa)</u> <u>(28 days' curing)</u>
Example 1	0.40		0.33
	0.49		0.45
	0.58		0.55
	0.50		0.46
	0.44		0.50
Average	0.48	Average	0.46
Example 2	0.42		0.33
	0.39		0.39
	0.48		0.38
	0.35		0.40
	0.37		0.44
Average	0.40	Average	0.39

From Table 1 it emerges that the average interfacial bond strengths of the fibres treated according to Example 1 (Invention) were 0.48MPa and 0.46MPa respectively after 7 and 28 days' curing. The corresponding values for Example 2 (Control) were respectively 0.40MPa and 0.39MPa, respectively showing an increase of 20% after 7 days' curing and of 18% after 28 days' curing, compared with the control.

### **EXAMPLE 3 - INVENTION**

Example 1 was repeated using polypropylene fibres which were formed from fibrillated polypropylene tape produced by extrusion followed

by a fibrillation process. The fibres had a nominal rectangular cross-section of 0.097mm x 7.5mm, being 36mm in length, with a specific gravity of 0.91, a tensile strength of 128MPa and an elongation at break of 5.3%.

#### **EXAMPLE 4 - CONTROL**

Example 2 was repeated using the fibrillated fibres of Example 3.

A proprietary cementitious mixture, Concor HT Wetcrete, obtained from Concor Technicrete (Proprietary) Limited, of 13 Church Street, Crown Industrial Area, Johannesburg, South Africa was prepared to form a shotcrete mixture and was admixed with fibrillated fibres whose surfaces had been activated in accordance with Examples 3 and 4 respectively.

The constituents of the mixture, including the aggregate and fibres, were admixed in a mechanical mixer which was connected to a spray nozzle by means of a peristaltic conveyor system. The proportion of fibres admixed with the shotcrete amounted to 9kg fibres/m<sup>3</sup> shotcrete. As soon as the mixture became homogeneous (i.e. after it was mixed for a period of about 4 minutes) it was passed along the peristaltic conveyor system and sprayed through the spray nozzle into a mould to spray-cast a square panel or plate having sides of 600mm and a thickness of 100mm. After the spray-casting, the panel or plate was left in the mould under air for 3 days, after which the panel or plate was water-cured for 25 days before energy-absorption tests were conducted on the panel or plate.

The energy-absorption tests were carried out by supporting each panel or plate along its 600mm edges while centre-point-loading was applied thereto over a central square area having sides of 100mm, respectively parallel to the 600mm sides of the panel or plate. The load was applied to the face of each panel or plate opposite to the direction from which the mixture arrived in the mould from the spray nozzle, i.e. the load was applied to the face of the panel or plate which, during the spray-casting, had rested on and abutted on the 600mm x 600mm floor of the mould which faced upwardly, the spraying taking place downwardly from the spray nozzle into the mould and on to the floor.

The panel or plate containing the fibres whose surfaces had been surface-activated in accordance with Example 3 was found to display a total energy absorption of 1096 joules(J), whereas the control panel or plate whose fibres had been surface-activated in accordance with Example 4 was found to display a total energy absorption of 688 J, i.e. the use of the activation atmosphere of Example 3 led to an increase of 59% in energy absorption of the panel or plate, compared with Example 4. Furthermore, while the load-bearing capacity of the latter panel or plate was found to decrease from 67kN, progressively over a deformation range of 5-25mm to a value of 7kN, the load-bearing capacity of the former was found to decrease at a slower rate from 54kN, progressively over the same deformation range to a value of 26kN. Thus, the panel containing fibres activated in accordance with Example 3 (invention) had a 3.7 times higher residual load-bearing capacity than the control panel whose fibres had been activated in accordance with Example 4.

### COATING OF SUBSTRATES

With regard to Examples 5 - 10 set out hereunder, a reactor-grade thermoplastic olefin (RTPO) SP 179-22 manufactured by Montell, was used, except where other polymers are specified. This RTPO consists of isotactic polypropylene polymerized together with a reactor-made ethylene-propylene rubber (EPR).

Various oxyfluorination atmospheres were used and degreasing of the substrate took place before oxyfluorination by washing it with water and a detergent before rinsing it with water, followed in some cases by wiping it with isopropanol. In this regard the Applicant has found that the nature of the detergent is not critical, and a number of household detergents were found to be suitable. The fluorination took place at room temperature, typically 25°C, for various periods of time. In each case the hydrolysed surface, after drying if necessary, was painted.

In the tests whose results are set out in Tables 2, 3 and 4 hereunder, the following paint was applied:-

A single-component polyurethane base coat in an organic solvent, obtained from Herberts (France) S.A., B.P. 1025, 78205, Nantes, La Jolie, Cedex, France, was used as a pigmented base-coating paint with the trade designation HERBERTS BN RG/PERSAN 777, RN 313.565 (Ref. No. FA 9211036) followed by a two-component unpigmented clear coat paint with the trade designation VERNIS

2-K EC 510027 (Ref. No. 9213226/FA 9213227) and a hardener designated FA 9212586. In each case two layers of base coat, each layer being at least  $2\text{ }\mu\text{m}$  thick and the thickness of the layers amounting in total to at most about  $15\text{ }\mu\text{m}$  thickness, were applied followed by two layers of clear (top) coat, each of about  $15 - 40\text{ }\mu\text{m}$  thickness. Each of the base coat layers was allowed to dry by leaving it exposed to air at room temperature for a period of 3 - 12 minutes, before the following layer was applied; and each layer was applied by spray-painting. The final layer was allowed to dry for 10 minutes and then baked at  $80^{\circ}\text{C}$  for 30 minutes. The final layer was exposed to the air at room temperature for a period of 3 days before the pull-off tests were performed.

In the tests whose results are set out in Tables 5 and 6 hereunder the following paint was applied:-

A two-component polyurethane pigmented top coat obtained from Dulux AECI Paints (Proprietary) Limited, ALRODE, 1451, Gauteng Province, South Africa. This white-pigmented top coat paint with the trade designation DUCO DURATHANE K Enamel Cathkin White/Wit (Ref. No. D 928-0025) and a hardener designated Slow D 928-0809 were used. In each case four layers of the two-component top coat were applied, amounting to approximately  $50\text{ }\mu\text{m}$  in total thickness. After the application of each layer, a flash-off period of 3 - 12 minutes was allowed before the following layer was applied. The final layer was allowed to dry for 10 minutes. The final layer was exposed to the air at room temperature for a period of 3 days before the pull-off tests were performed.

Water contact angles were measured, using a Cahn DC A 322 instrument obtained from MET Systems, 3 Gaiety Street, Robindale, Randburg, Gauteng Province. The advancing and receding angles were measured as described in the Cahn DCA operating manual, using a stage speed of  $50\mu\text{m/s}$ .

Adhesion of the paint to the substrate was tested by adhesively securing metal-backed test pads to the painted substrate, using a cyanoacrylate adhesive available from Loctite (South Africa) (Proprietary) Limited under the trade designation of LOCTITE 496 CYANOACRYLATE. Pull-off adhesion strength was tested in accordance with International ISO Standard 4622-1978(E), using a 20 mm diameter test cylinder adhesively secured to the painted surface using said Loctite 496. The test cylinders were pulled from the painted test samples by means of a tensile tester, the force in Newtons (N) required to break the test assembly was recorded together with the standard deviation. The breaking strength in megapascals (MPa) is given by  $F/314$ , where  $F$  is the breaking force in Newtons, and the test cylinders were 20 mm in diameter. The fracture surfaces were examined and the results were expressed as the percentage area and in terms of the site of the fracture, expressed in terms of adhesive-, cohesive- or adhesive/cohesive failure. In Tables 4 - 9 the following scheme was used to describe the site of fracture:

- A = Cohesive failure of the substrate
- A/B = Adhesive failure between substrate and first coat
- B = Cohesive failure of first coat
- B/C = Adhesive failure between first and second coats



-/Y = Adhesive failure between final coat and adhesive.

In Examples 5 - 10 a single-component paint is referred to as a 1-K paint, and a two-component paint is referred to as a 2-K paint.

#### EXAMPLE 5

Samples in the form of plates made of the RTPO SP 179-22 having dimensions of  $10 \times 10 \text{ cm}^2$  were exposed to an oxyfluorinating gas mixture at  $25^\circ\text{C}$  in a reaction vessel after evacuating the vessel to a residual pressure of 25 kPa air. Said oxyfluorinating gas mixture was charged into the vessel at a total pressure of 30 kPa. The charged vessel thus contained a mixture made up of humid ambient air with a partial pressure of 25 kPa, and an  $\text{F}_2/\text{N}_2$  gas mixture at a partial pressure of 5 kPa, the  $\text{F}_2/\text{N}_2$  mixture comprising 20% by volume  $\text{F}_2$  and 80% by volume  $\text{N}_2$ . This gas mixture will be referred to hereunder as '5kPa 20%  $\text{F}_2/\text{N}_2/25\text{kPa}$  air mixture'. Oxyfluorinating times were varied from a minimum of 5 seconds up to a maximum of 1 hour (3600 seconds), to obtain various different surface concentrations of fluorine on the treated surface. Two layers of Herberts BN RG Persan base coat were applied followed by two layers of clear coat. The four layers had an approximate thickness of  $52\mu\text{m}$ . The painting took place after exposing the oxyfluorinated samples for 24 hours at  $25^\circ\text{C}$  to ambient air to hydrolyse the oxyfluorinated

surfaces. The standard deviation measured during the evaluation of the paint adhesion strength was about 1,4 MPa. Results are set forth in the following table, Table 2.

**TABLE 2**

SP 179-22 material exposed at 25°C to 5 kPa 20% F<sub>2</sub>/N<sub>2</sub>/25 kPa air mixture painted with Herberts Persan 1-K base coat/2-K clear coat, after exposing the surface to air for 24 h.

Oxyfluorinating time (seconds)	Breaking force (MPa)	Nature of failure	Fluorine concentration ( $\mu\text{gF}/\text{cm}^2$ )	Water contact angle advance/recede (°)
0	0	100A/B	0	108,7/77,0
5	5,39	60A,40A/B	2,9	92,1/51,7
10	4,84	80A,20A/B	2,9	91,2/43,8
15	5,06	90A,10A/B	3,0	75,5/34,2
60	6,59	100A	3,2	63,4/25,8
300	6,74	100A	3,8	56,5/19,9
900	6,25	80A,20A/B	4,3	43,9/15,4
1800	6,54	100A	4,8	65,5/20,2
3600	6,64	80A,20A/B	6,4	67,7/20,5

From Table 2 it is clear that excellent surface activation and paint adhesion are obtained from a 5 second exposure time onwards and that no decrease in the adhesion strength is observed for longer times, even after 1 hour of oxyfluorination. Although very little change in the

amounts of surface- incorporated fluorine is observed, initial changes in the water contact angle are sensitive measures for adequate activation. A surprisingly small amount of fluorine is incorporated in the surface.

### EXAMPLE 6

Example 5 was repeated except that the painted samples were immersed in water at 40°C for 10 days before the paint adhesion strength was evaluated. The standard deviation in the breaking force was about 2,0 MPa. Results are set forth in the following table, Table 3:

TABLE 3

SP 179-22 material exposed at 25°C to 5 kPa 20% F<sub>2</sub>/N<sub>2</sub>/25 kPa air mixture painted with Herberts Persan 1-K base coat/2-K clear coat after 24 hours exposure to air, followed by 10 days of immersion in water at 40°C.

Oxyfluorinating time (seconds)	Breaking strength (MPa)	Nature of failure
5	5,10	90A,10A/B
10	6,90	100A
15	6,59	100A
60	5,89	100A
300	8,21	100A

900	11,61	100-/Y
1800	7,97	100-/Y
3600	4,38	100A

From comparing the paint adhesion strength before water immersion (Table 2) to that after immersion (Table 3), it is clear that no decrease arising from the immersion is observed. In fact, an increase was generally observed.

#### EXAMPLE 7

Using the same material, oxyfluorination and painting conditions as for Example 5, but with an oxyfluorinating time of 10 seconds, the influence of different partial pressures of fluorine was investigated. The results are summarized in Table 4 hereunder.

From Table 4 one can deduce that a partial pressure of 1kPa of  $F_2$  (5kPa 20%  $F_2/N_2$ /25kPa air mixture) is adequate to induce excellent adhesion strength.

TABLE 4

Material SP 179-22 exposed at 25°C to various mixtures of  $F_2/N_2$  and air with the air at 25kPa and the  $F_2/N_2$  at various different pressures

for 10 seconds and then painted with Herberts Persan 1-K base coat/2-K clear coat after exposure to air for 24 hours.

Pressure of 20% $F_2/N_2$ added to 25kPa Air Mixture (kPa)	Breaking Strength (MPa)	Nature of Failure	Water Contact Angle (°) Advance/Recede
1	No adhesion	No adhesion	100/72,9
2	No adhesion	No adhesion	100/58,0
5	7,09	10A, 90A/B	64,8/30,5
10	6,54	100-/Y	68,7/29,3
20	8,62	40A/B, 60-/Y	60,5/20,2
30	11,38	100-/Y	59,7/24,4
40	9,44	100-/Y	62,2/23,2

### EXAMPLE 8

As for Example 5, all SP 179-22 plate samples were oxyfluorinated for 10 seconds using 5 kPa 20%  $F_2/N_2$ /25kPa air mixture, at different temperatures. The paint adhesion of the samples was evaluated after 10 days of water immersion at 40°C. The results are summarised in Table 5.

From Table 5 it is clear that good adhesion is obtained over a wide oxyfluorination temperature range, but that adhesion decreases substantially when oxyfluorinating near the melting temperature (169°C) of the plastic substrate. Comparing the 70.3° contact angle at 150°C

with that of Table 2, it was to have been expected that excellent adhesion would be achieved. This indicates that contact angle changes are not sufficient to predict adequate adhesion after water immersion.

**TABLE 5**

Material SP 179-22 oxyfluorinated at a number of different temperatures by exposure to 5 kPa 20% F<sub>2</sub>/N<sub>2</sub>/25kPa air mixture for 10 seconds and then painted with Dulux Cathkin White after exposure to air for 24 hours.

Oxyfluorination temperature (°C)	Breaking strength (MPa)	Nature of failure	Fluorine Concentration (μgF/cm <sup>2</sup> )	Water contact angle (°) advance/recede
25	7,66	10A,90A/B	2,7	63,0/34,6
50	9,24	10A,90-/Y	2,9	60,8/34,1
100	7,60	50A,50A/B	3,2	53,5/32,2
150	No adhesion	No adhesion	2,9	70,3/37,1

**EXAMPLE 9**

Using the same oxyfluorination conditions as for Example 5 but fixing oxyfluorinating time at 10 seconds and using a 5 kPa 20% F<sub>2</sub>/N<sub>2</sub>/25 kPa air mixture, an SP 179-22 sample was oxyfluorinated. Instead of waiting for 24 hours before painting, the sample was painted with Dulux Cathkin White after exposure to the atmosphere, on the one hand, 600 seconds after oxyfluorination, and, on the other hand, 7 months

after fluorination. The paint adhesion was evaluated after the painted sample was submerged for 10 days at 40°C in water - See Table 6, Samples Nos 1 and 2 hereunder.

Comparing the adhesion strength with that of a sample painted after 24 hours after oxyfluorination (e.g. adhesion strength of 7,66 MPa at 25°C in Table 5) it is clear that paint adhesion strength is not influenced by hydrolysis time of the substrate before painting.

Painting the oxyfluorinated sample after 7 months of exposure to the atmosphere had no detrimental effect on adhesion strength, as is apparent from a comparison of the respective breaking strength values of 6.7 MPa and 6.8 MPa, respectively of Sample 1 for 600 seconds and Sample 2 for 7 months in Table 6 hereunder. This result shows that surface oxyfluorination can be regarded as permanent.

To determine whether or not the paint adhesion strength deteriorates with time, an SP 179-22 sample, Sample 3 in Table 6 hereunder, was oxyfluorinated in the same fashion as for Samples 1 and 2. Sample 3 was exposed to air for 24 hours after oxyfluorination, before being painted with Herberts Persan 1-K base coat followed by a 2-K polyuréthane clear coat (see paint system (a) in Example 7 hereunder). After one year's exposure to the laboratory atmosphere the paint adhesion strength was determined and a value of 10.3 MPa was

obtained (see Sample 3 in Table 6) indicating that no loss in paint adhesion strength took place after one year. Indeed, samples submerged for 3 months in water at 50°C, did not show any decrease in paint adhesion strength.

**TABLE 6**

Material SP 179-22 exposed at 25°C to a 5 kPa 20% F<sub>2</sub>/N<sub>2</sub>/25 kPa air mixture for 10 seconds, and then painted with Dulux Cathkin White and evaluated after different exposure times.

Sample No	Breaking strength (MPa)	Nature of failure	Fluorine Concentration (µgF/cm <sup>2</sup> )	Water contact angle (°) advance/recede
1	6,7 <sup>(1)</sup>	10A,90A/B	2,5	63,1/34,6
2	6,8 <sup>(2)</sup>	20A,50A/B, 30-/Y	Not measured	Not measured
3	10,3 <sup>(3)</sup>	100-/Y	Not measured	Not measured

<sup>(1)</sup> Painted 10 min after surface oxyfluorination

<sup>(2)</sup> Painted 7 months after surface oxyfluorination

<sup>(3)</sup> Breaking strength evaluated one year after painting

### EXAMPLE 10

For this example a number of different polyolefin substrates, known to be difficult to paint, were oxyfluorinated and painted



with a variety of different paints. The following substrates were oxyfluorinated:

- (a) A reactor-grade polypropylene SP 179-22 manufactured by Montell and obtained from Bruneal Plastics (Proprietary) Limited, PO Box 289, Lonehill 2062, Gauteng Province;
- (b) A block copolymer manufactured by Plastomark (Proprietary) Limited of Highchem Park, 16th Road, Midrand, Gauteng Province, Republic of South Africa;
- (c) A polypropylene homopolymer from Polifin Limited, PO Box 72, Modderfontein, 1645, Republic of South Africa;
- (d) A random or statistical polypropylene copolymer called Stat from Plastomark (Proprietary) Limited;
- (e) A high density polyethylene (HDPE) manufactured by BASF South Africa (Proprietary) Limited, 852, 16th Street, Midrand (Designation Lupolen 526125).
- (f) A linear low density polyethylene manufactured by Polyfin Limited (Rotational moulding grade 3185).

These olefin substrates were oxyfluorinated by exposing them at 25°C to a partial pressure of 5 kPa 20% F<sub>2</sub>/N<sub>2</sub>/25 kPa air mixture for 10 seconds and then painting them after 24 hours exposure to air with the following

paints i.e. spray-painting the surface by applying one of the following paint systems:

- (a) A 1-K polyurethane base coat with the trade designation Herberts BN RG Persan 777 RN (RN 313. 565) followed by a 2-K polyurethane clear (top) coat with the trade designation VERNIS 2-K EC 510027 (Ref. No. 9213226/FA 9213227) and a hardener (Ref. No. FA 9212586).
- (b) A 2-K top coat with the trade designation DUCO DURATHANE K ENAMEL Cathkin White (Ref. No. D 928-0025) obtained from Dulux (Proprietary) Limited, PO Box 911641, 117 Phillips Street, Rosslyn, Pretoria, Gauteng Province.
- (c) An Epoxy 2-K paint with the trade designation Dulux Hi Chem Epoxi-Emalje Brilliant Green (Ref. No. D 355-0221) and a hardener (Ref. No. 39490) obtained from Dulux (Proprietary) Limited.
- (d) A 1-K water-borne base coat (WBC), followed by the 2-K clear coat mentioned in (a) above, from Herberts.
- (e) A 2-K soft-touch coat, trade designation Karl Wörwag, Wöropur-Softfeellack Schwartz Nach Matt (Ref. No. 64090) mit Hartner (Ref. No. 57859) obtained from Karl Wörag Lack- und Farbenfabrik GmbH & Co, Strohgän Strasse 28, 70435 Stuttgart,

Germany.

- (f) A 1-K primer trade designation Plascon 1-K A/Dry H/Build Pri for P/Propyl. EPDM obtained from Plascon (Herberts), PO Box 1594, Port Elizabeth 6000, Eastern Cape Province, Republic of South Africa.

From Table 7 hereunder it can be seen that oxyfluorinations ((a)-(f)) generally led to improved paint- and primer adhesion when compared to the adhesion of a primer on a surface that had not been oxyfluorinated. Polymers containing propylene (RTPO SP 179, block copolymer, homopolymer, and random copolymer) showed better adhesion than those containing only ethylene (HDPE, LLDPE). The adhesion of paints applied directly to an oxyfluorinated surface was in most cases equal or better than the adhesion of primers on an oxyfluorinated surface.

It should be noted that the water-based or water-borne base coat (d) could be applied directly to the oxyfluorinated surface without first applying a primer. Thus, the use of adhesion promoters is not necessary when substrates are oxyfluorinated before paint application. This can eliminate the cost of applying expensive, environmentally unfriendly primer coats. This fact, as well as the excellent adhesion

obtained on an oxyfluorinated substrate with a water-borne base coat, can significantly reduce painting costs and reduce health risks for workers applying paints.

The soft-touch paint ((e) in Table 7) showed excellent adhesion to polypropylene-containing polymers. Soft-touch paints are generally applied to highly isotactic polypropylene block copolymers used for the interior trims and dashboards of motor cars. From Table 7 it can be seen that the adhesion of the soft-touch paint was excellent on the block copolymer.

TABLE 7

Various olefin polymers exposed at 25°C to 5 kPa 20% F<sub>2</sub>/N<sub>2</sub>/25 kPa air mixtures for 10 seconds and then painted after 24 h with various paints. (g) Shows the breaking strength of the primer when applied to the various olefins not oxyfluorinated.

Paint type	Manufacturer	RTPO SP 179-22		Block copolymer		Homopoly mer		Random copolymer		HDPE		LLDPE	
		Breaking strength MPa	Nature of failure	Breaking strength MPa	Nature of failure	Breaking strength MPa	Nature of failure	Breaking strength MPa	Nature of failure	Breaking strength MPa	Nature of failure	Breaking strength MPa	Nature of failure
(a) 1-K base/2-K clear polyurethane	Herberts	4,7 ± 1,4	90A, 10A/B	9,5 ± 2,4	100-Y	6,9 ± 2,2	100A	5,5 ± 0,6	100A	4,2 ± 1,0	100A/B	2,1 ± 0,3	100A/B
(b) Polyurethane 2-K top coat	Dulux	6,7 ± 2,0	10A, 90A/B	13,4 ± 2,1	10A, 90-Y	10,4 ± 4,0	100A/B	6,1 ± 2,4	20A 80A	2,5 ± 1,4	100/B	1,5 ± 0,6	100A/B
(c) Epoxy 2-K	Dulux	6,9 ± 0,8	100B/C	7,3 ± 0,6	100B/C	7,8 ± 1,3	100B/C	5,7 ± 0,2	100A	3,3 ± 1,0	100A/B	1,8 ± 0,6	100A/B
(d) WBC/2-K clear	Herberts	6,8 ± 2,1	100A/B	9,8 ± 1,1	50B, 50A/B	5,2 ± 1,5	100B/C	6,1 ± 2,4	20A, 80A/B	4,4 ± 1,0	100A/B	1,8 ± 0,4	100A/B
(e) Soft touch	Wörrwag	5,0 ± 1,5	2 0 A 30A/B 50-Y	7,4 ± 1,7	100-Y	7,8 ± 1,6	60A, 4-Y	8,5 ± 2,8	20A/B 80-Y	3,3 ± 0,8	100A/B	1,3 ± 0,3	100A/B
(f) 1-K Primer/polyurethane 2-K top coat	Plascon/Dulux	5,3 ± 1,2	70A, 30A/B	5,4 ± 0,6	100A/B	4,9 ± 1,1	100A/B	5,06 ± 0,7	100A/B	3,8 ± 1,2	100A/B	1,7 ± 0,2	100A/B
(g) Same as (f), but substrates unfluorinated	Plascon/Dulux	2,8 ± 0,5	100A/B	1,1 ± 0,2	100A/B	3,23 ± 1,0	100A/B	3,1 ± 1,0	100A/B	1,2 ± 0,2	100A/B	0,9 ± 0,2	100A/B

From the results in the Examples 5 - 10 it appears that the process of the present invention is capable of producing products with regard to which substantial breaking forces are required to break the bond between the oxyfluorinated surface of the substrate, and the first or lowermost paint layer applied thereto. Typically failure takes place either under the oxyfluorinated surface, in the material of the substrate, or at the outer surface of the paint, at the interface between the paint and the adhesive. In none of the tests was more than 40% of the site of the failure made up of adhesive failure between the oxyfluorinated substrate surface and the first or lowermost coat of paint. Furthermore in each of Examples 5 - 10, depending on the exposure times, results could be achieved where no such adhesive failure at the sample/paint interface took place.

In particular it is to be noted that the humid ambient air (usually between 30% and 70% relative humidity) of the 5kPa 20%  $F_2/N_2$ /25kPa air mixture employed in Examples 5 - 10 contained sufficient humidity for the 5kPa 20%  $F_2/N_2$ /25kPa air mixture to have a moisture content in terms of water vapour of 2 - 10 mg/l.

Further tests, as set forth hereunder in Examples 11 - 13, were carried out to compare dry oxyfluorination with oxyfluorination using the gas/vapour mixture oxyfluorinating atmosphere of the present invention, containing water vapour. In Examples 11 - 13, the polypropylene homopolymer used was that listed under (c) in Example 10 above, and

a rotational moulded linear low-density polyethylene (LLDPE) obtained from Sasol Polymers, a division of Sasol Limited, Johannesburg, under the trade designation Reference LLDPE HR 486/06.

Sample preparation was done in accordance with that described above for Examples 5 - 10 except that, instead of wiping with isopropanol, the samples were left to dry overnight. The paint used was the DUCO DURATHANE K ENAMEL Cathkin White/Wit (Ref. No. D 928-0025) top coat paint/Slow D 928-0809 hardener combination from Dulux AECI Paints (Proprietary) Limited referred to above. When an epoxy adhesive is referred to in Examples 11 - 13 it is that available from Pratley Manufacturing & Engineering Company (Proprietary) Limited, Fatoria, Krugersdorp, P.O. Box 3055, Kenmare 1745 Gauteng Province, South Africa, under the trade designated Pratley Quickset White Epoxy Glue, which was used in accordance with the manufacturer's instructions. Adhesion was evaluated using the metal-backed test pads to measure pull-off and adhesion strength using a 20mm diameter test cylinder according to International ISO Standard 4622-1978(E) as described above. Samples in the form of  $10 \times 10\text{cm}^2$  plates of the polymers described in Examples 11 - 13 were exposed to various oxyfluorinating gas/vapour mixtures according to the invention at  $25^\circ\text{C}$  in a reaction vessel. The atmospheric relative humidity of the ambient air used was 50 - 70% during the course of carrying out Examples 11 - 13.

The apparatus of Figure 2 was used to create a gas/vapour mixture as an oxyfluorinating atmosphere having a desired relative humidity in a reaction vessel.

In particular a humid oxyfluorination atmosphere of about 75% relative humidity and a dry oxyfluorination atmosphere of substantially 0% relative humidity were created.

In Figure 2, the apparatus employed is generally designated by reference numeral 22. The apparatus comprises a reactor in the form of a stainless steel reaction vessel 24 shown provided with a lid 26 sealed by means of an O-ring 28. The reaction vessel 24 is provided with a heater jacket 30, and is connected via an inlet/outlet opening 32 in its lid 26 to a fluid flow line 34. The flow line 34 is provided with a pair of shut-off valves, respectively designated 36 and 38, joined together by a flexible metal bellows 40.

Flow line 34 branches from a manifold 42, to which are connected a plurality of flow lines respectively designated 44, 46, 48 and 50.

Flow line 44 leads to a vacuum pump 52, and is separated from the remainder of the manifold 42 by a shut-off valve 54. Flow lines 46, 48 and 50 enter the manifold 42 on the same side of the valve 54 as the flow line 34, i.e. remote from the flow line 44.



Flow line 46, provided with a regulating valve 56 is a supply line for a mixture of  $F_2/N_2$ ; and flow line 48, provided with a regulating valve 58 is a dry synthetic air supply line. In turn, the flow line 50 is provided with a shut-off valve 60 and a regulating valve in the form of an adjustable needle valve 62 and leads to a gas-wash bottle 64, containing water 66 and provided with an air inlet pipe 68. Finally, a pressure transducer 70 is shown connected to the manifold 42 by a pressure line 72.

In other words the reactor 24 is a stainless steel vessel sealed by the O-ring 28. The temperature in the reactor is controlled by the heater jacket 30. For convenience valves 36 and 38 are joined by the flexible metal bellows 40. The glass gas-wash bottle 64 containing water 66 is used to humidify the air loaded into the fluorination reactor 24. Two valves 60, 62 are used at the point where the humidified air from the gas-wash bottle 64 is admitted to the manifold 42. Valve 62 is an adjustable needle valve that is set to deliver humidified air to the evacuated reactor 24 at a rate which results in a level of humidity of at least 75% relative humidity. Valve 60 is a shut-off valve, which is used to admit/shut-off the humid air flow into the manifold 42 and the reactor 24.

Vacuum pump 52 is connected to manifold 42 via the normally closed valve 54 and is used to evacuate the manifold 42 and reactor 24

before each run. The pressure transducer 70 constantly measures the pressure in the manifold 42 and reactor 24 of the apparatus 22 to control the steps of evacuation of the reactor 24 and subsequent loading of gas components from flow lines 46, 48 and 50. Valve 58 admits the  $F_2/N_2$  mixture via line 46 to the manifold 42 and is used to admit and regulate the loading of the  $F_2/N_2$  mixture before the oxyfluorination process. During humid oxyfluorination air/water vapour mixture from gas-wash bottle 64 is loaded via the manifold 42 into the reactor 24 by opening valve 60 and adjusting valve 62 to achieve a desired loading rate. Instead, for dry oxyfluorination, dry synthetic air from a synthetic air cylinder (not shown) attached to supply line 48 using a flexible metal hose (also not shown) is fed via its own flow regulation valve (not shown) and valve 58 into the manifold 42. The synthetic air was purchased from Air Products (Proprietary) Limited, Kempton Park with the following specification:

- a) Oxygen - 20 - 22% by volume
- b) Nitrogen - the balance
- c) Water - Less than 2 ppm

#### HUMID OXYFLUORINATION PROCEDURE

In operation the temperature of the reactor 24 was regulated at about 1 - 2°C above ambient temperature by means of the heater jacket 30. The actual recorded temperatures during the test runs fluctuated

between 25°C and 30°C. Initially valves 36, 38, 60, 54, 58 and 56 were closed and the test samples were loaded into the open reactor 24. The lid 26 of the reactor 24 was then closed and sealed by means of O-ring 28. Valves 54, 36 and 38 were then opened and the manifold 42 and reactor 24 of the apparatus 22 were evacuated to as low pressure as possible whereafter valve 54 was closed. Valve 60 was then opened and humid air was admitted into the manifold 42 and reactor 24 at a desired rate by means of needle valve 62 to allow air of about 75% or more relative humidity into the reactor 24 up to a specified pressure. Valve 60 was then closed. The  $F_2/N_2$  mixture from line 46 was then admitted up to a specified pressure in the manifold 42 and reactor 24, by slowly opening valve 56. Thereafter, valves 56, 38 and 36 were closed for the duration of the humid activation.

The test samples were left in contact with the gas mixtures for specified periods of time. Valves 54, 38 and 36 were then opened and the gases in the reactor 24 pumped off. Valve 54 was then closed and air from the atmosphere was admitted to the manifold 42 and reactor 24 by opening valve 60. When the pressure in the manifold 42 and reactor 24 reached about 80kPa, valve 60 was closed and valve 54 was opened to allow pump 52 to pump air out of the manifold 42 and reactor 24. This cycle of evacuation and flushing with air was repeated three times in order to remove any residual fluorine and hydrofluoric acid from the reactor 24. Finally, air was allowed into the reactor 24 through valve 60

up to atmospheric pressure whereafter the lid was opened and the test samples removed from the reactor.

### **DRY OXYFLUORINATION PROCEDURE**

The only difference between dry and humid oxyfluorination was the use of dry synthetic air from the synthetic air bottle attached to line 48, instead of humid air from the gas-wash bottle 64. Special precautions were, however, taken in removing any moisture in the apparatus 10 therefrom, downstream of valve 60 before, during and after the dry oxyfluorination process.

The temperature of the reactor was controlled as before. Valves 36, 38, 60, 54, 58 and 56 were closed as before. Thereafter the apparatus was evacuated, followed by flushing to a pressure of about 80 kPa with dry synthetic air from the air supply connected to line 48 by manipulating valves 54 and 58 in succession. This was repeated three times in order to remove any traces of water from the manifold 42 and reactor 24. Dry air was then bled into the manifold 42 and reactor 24 up to atmospheric pressure, before closing all valves and opening the reactor lid 26. Pre-dried test samples were then quickly loaded into reactor 24, whereafter the reactor lid 26 was replaced and sealed with O-ring 28. A sequence of three successive evacuations, each followed by flushing with synthetic dry air to about 80 kPa, of the manifold 42

and reactor 24 was performed as before, to remove all traces of moisture therefrom. Finally, dry synthetic air was admitted to the manifold 42 and reactor 24 up to a specified pressure via valve 58. Valve 56 was then slowly opened and  $F_2/N_2$  mixture admitted to the manifold 42 and reactor 24 to a specified partial pressure. Valves 56, 38 and 36 were then closed for the duration of the dry activation.

The test samples were left in contact with the oxyfluorination atmospheres for specified periods of time. Valves 54, 38 and 36 were then opened and the gases in the reactor 24 and manifold 42 evacuated therefrom by pump 52. The manifold 42 and reactor 24 were then flushed with synthetic dry air and evacuated three times as before to remove all residual fluorine and hydrofluoric acid. Finally, synthetic dry air was allowed to flush the reactor 24 through valve 58 up to atmospheric pressure whereafter the lid 26 was opened and the test samples were removed from reactor 24.

#### **EXAMPLE 11**

Polypropylene homopolymer samples were cleaned and were subjected to dry oxyfluorination in the absence of water vapour, and to humid oxyfluorination in the presence of water vapour. The samples subjected to dry oxyfluorination were left for 24 hours in a silica gel-filled

desiccator prior to oxyfluorination, whereas those subjected to humid oxyfluorination were equilibrated in a closed vessel with a relative humidity of  $\geq 95\%$  prior to oxyfluorination. All samples were oxyfluorinated for 10 seconds. For the dry oxyfluorination, samples were exposed to an oxyfluorinating gas atmosphere consisting of a  $F_2/N_2$  gas mixture at a partial pressure of 3 kPa, the  $F_2/N_2$  mixture comprising 20% by volume  $F_2$  and 80% by volume  $N_2$ , and dry air consisting of an  $O_2/N_2$  mixture comprising 21% by volume  $O_2$  and 79%  $N_2$  by volume, at a partial pressure of 25 kPa. The total reaction pressure was thus 28 kPa, and the atmosphere comprised 3 parts by volume of the  $F_2/N_2$  mixture, mixed with 25 parts by volume of the  $O_2/N_2$  mixture. For the humid oxyfluorination the atmosphere was the same, except that the dry air was replaced by air comprising  $O_2$  and  $N_2$  in the same 21:79 volume ratio, but of 75% relative humidity. The results are set forth in Table 8.

**TABLE 8**

2-K polyurethane paint adhesion strengths on dry- and humid oxyfluorinated polypropylene samples. Samples were painted within 1 hour of oxyfluorination.

Dry OxyfluorinationHumid Oxyfluorination

Breaking Strength (MPa)	Nature of Failure	Breaking Strength (MPa)	Nature of Failure
9.88	100% A/B	13.62	90%-/Y, 10% A/B
13.82	100% -/Y	9.73	90%-/Y, 10% A/B
4.49	100% A/B	11.40	90%-/Y, 10% A/B
10.79	100% -/Y	12.18	90%-/Y, 10% A/B
7.35	50% A/B, 50% - /Y	13.79	100%-/Y
Mean 9.3 ± 3.5		Mean 12.1 ± 1.7	

It was noted that for the dry oxyfluorination the adhesive failure generally occurred between the polypropylene substrate and the paint coating, while for the humid oxyfluorination the failure was between the paint coating and the adhesive, indicating superior paint adhesion to the substrate when humid oxyfluorination was employed. This was emphasised by the significant increase in average breaking strength from 9.26 MPa to 12.14 MPa when dry oxyfluorination was replaced by humid oxyfluorination. This was coupled with a substantial decrease in standard deviation, suggesting that humid oxyfluorination is more homogeneous than dry oxyfluorination, leading to a more reliable activation of the substrate with the potential for better quality control. The nature of the failure for the humid oxyfluorination samples indicates that the A/B bond strength was in fact greater than the average value

of 12.14 MPa. Further tests showed that a drop from 75% to 65% relative humidity in the humid oxyfluorination gave a mean breaking strength of 12.43 MPa, which compared favourably with the 12.14 MPa in Table 8 for 75% relative humidity.

### **EXAMPLE 12**

Example 11 was repeated on rotational moulded linear low density polyethylene, with an increase of reaction time from 10 seconds to 3 minutes. Results are set forth in Table 9.

**TABLE 9**

2-K polyurethane paint adhesion strengths on dry - and humid oxyfluorinated linear low density polyethylene.

#### **Dry Oxyfluorination**

#### **Humid Oxyfluorination**

<b>Breaking Strength (MPa)</b>	<b>Nature of Failure</b>	<b>Breaking Strength (MPa)</b>	<b>Nature of Failure</b>
0.93	100% A/B	3.05	100% A/B
1.91	100% A/B	7.07	100% A/B
0.78	100% A/B	5.80	100% A/B
1.26	100% A/B	3.81	100% A/B
5.86	100% A/B	3.92	100% A/B
Mean 2.2 ± 2.1		Mean 4.7 ± 1.7	



With linear low density polyethylene changing from the dry oxyfluorination to the humid oxyfluorination effectively doubled the breaking strength with a substantial decrease in standard deviation. In each case failure occurred between the polyethylene substrate and the paint coating. As with Example 11, the increase in breaking strength achieved by humid oxyfluorination was substantial.

### EXAMPLE 13

Example 11 was repeated except that the paint coating of Example 11 was replaced by a coating of Pratley Quickset White Epoxy Glue. Results are set forth in Table 10.

TABLE 10

Pratley Quickset White Epoxy Glue adhesion strength on polypropylene homopolymer.

#### Dry Oxyfluorination

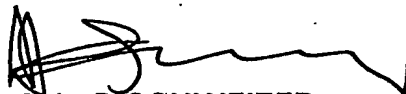
#### Humid Oxyfluorination

Breaking Strength (MPa)	Nature of Failure	Breaking Strength (MPa)	Nature of Failure
2.76	100% A/B	13.44	100% A
5.94	50% A/B, 50% A/B	13.93	100% A
13.33	100% A	12.19	100% A
5.16	50% A/B, 50% A	13.89	100% A
11.18	100% A		
Mean 7.7 ± 4.4		Mean 13.3 ± 0.8	

In Table 10 test results for certain samples were ignored and are excluded because of uneven sample surfaces which rendered these test results unreliable. In Table 10 A/B refers to adhesive failure between the polypropylene substrate and the epoxy coating, while A refers to cohesive failure of the substrate. The results shown in Table 10 also confirm that changing from dry oxyfluorination to humid oxyfluorination leads to an improvement of breaking strength for adhesive coatings as well as more homogeneous surface activation.

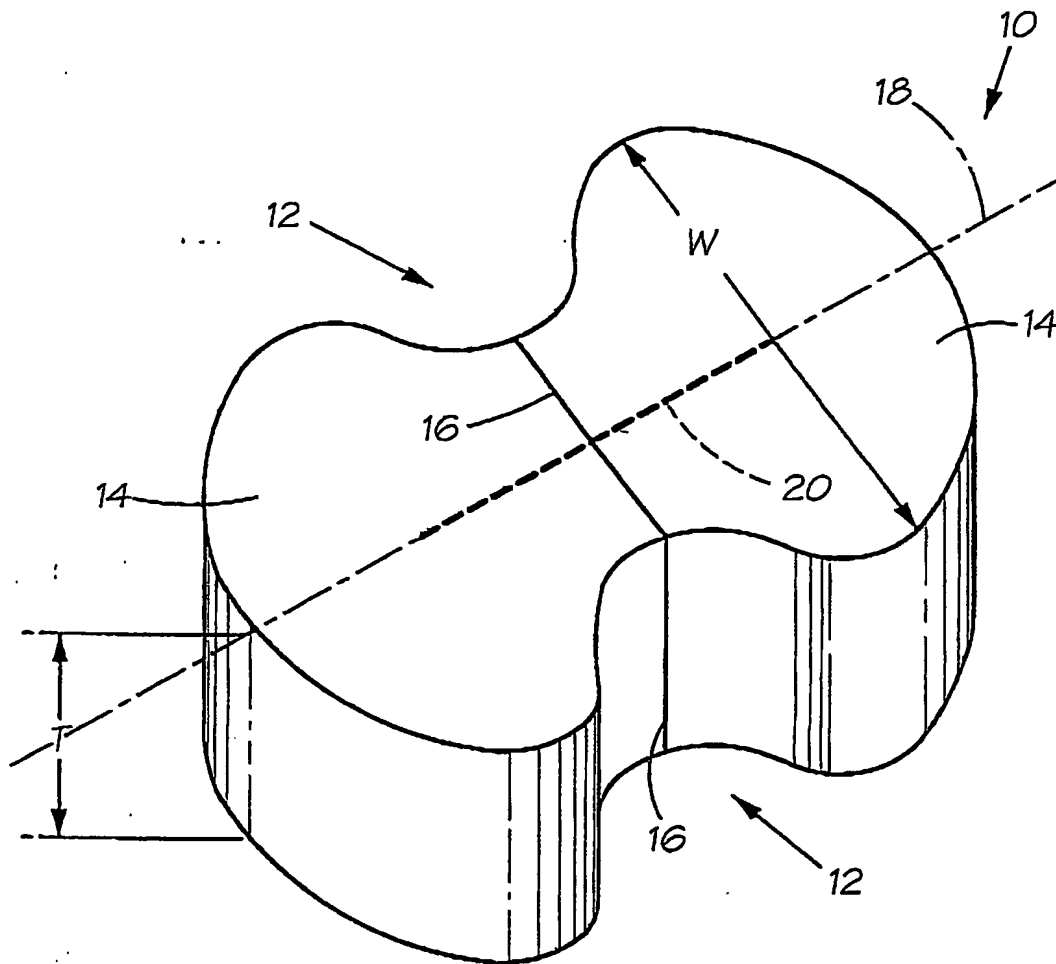
Here the epoxy coating also serves as the adhesive for securing the breaking strength test cylinder to the coating, so that no further adhesive is applied as in the case of paint coatings.


**DATED THIS 18th day of FEBRUARY 2003**



**AV vR SCHWEIZER  
ADAMS & ADAMS  
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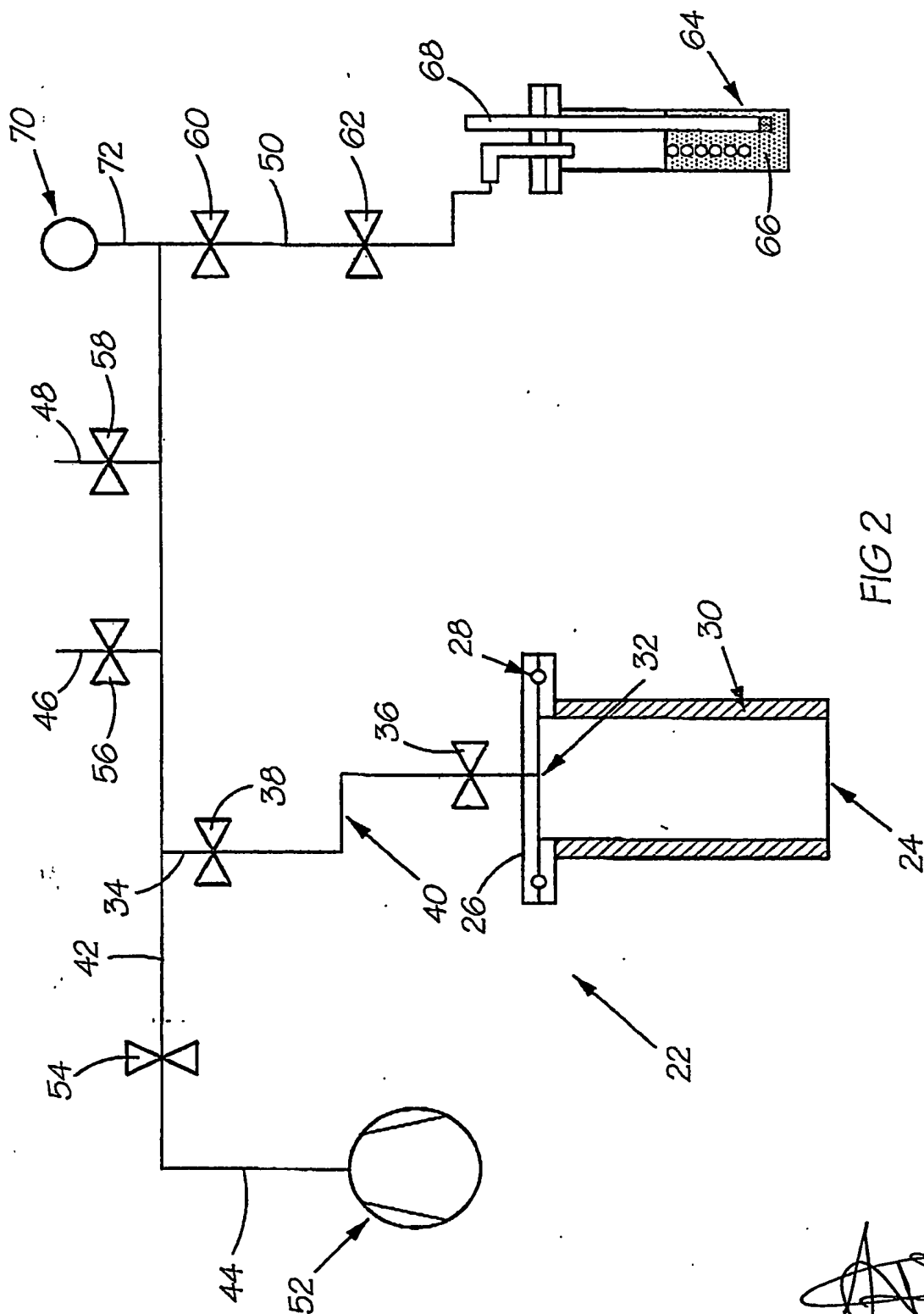


FIG 2

*[Signature]*  
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